EFFECT OF CHEMICAL COMBINATION ON X-RAY ABSORPTION

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PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF CORNELL UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

WALTER BERTRAM MOREHOUSE

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By W. B. Morehouse

Abstract

The x-ray absorption by aqueous solutions was measured before and after chemical reaction, employing a differential null method similar to that described by Becker (Phys. Rev. 20, 134, 1922). The direct and zirconium filtered beam from a water-cooled molybdenum Coolidge tube, operating at 30 kv peak, were used. Cells having equal compartments were used, so that the same elements were in the beam before and after combination.

Measurements were made on the following reactions:

(A) $KI+I_2+2Na_2S_2O_3 \rightarrow KI+2NaI+Na_2S_4O_6$.
(B) $K_2Cr_2O_7+12KI+14HCl \rightarrow 8KCl+2CrCl_3+3I_2+6KI+7H_4O$
(C) $NaOH+HCl \rightarrow NaCl+H_2O$.
(D) $KOH+HCl \rightarrow KCl+H_2O$.
(E) I_2 in 70 percent alcohol $+2Na_2S_2O_3 \rightarrow 2NaI+Na_2S_4O_6$.

Corrections having been made for changes in density the results indicate: Reaction (A); the mass absorption coefficient for the solution after reaction for direct beam approximately 0.24 percent less than before reaction; for filtered beam 0.36 percent less: Reaction (B); direct beam; 0.25 percent greater: Reaction (C); direct beam; no appreciable change: Reaction (D); direct and filtered; no appreciable change: Reaction (E); direct beam; 0.36 percent less. The results indicate that the mass absorption coefficient for an element depends upon its valence or state of chemical combination. Since iodine, sulphur and chromium are the only elements changing valence and since computations from known absorption coefficients show that the absorption by the iodine in the beam is several times that by either the sulphur or the chromium, its seems probable that the absorption by iodine in the free state is greater than its absorption in the combined state.

Introduction

Benoist,[1] from the result of his measurements on x-ray absorption, first stated that the x-ray absorption coefficient for an element is the same whether the element is in the free state or combined chemically with other elements. In fact one finds the same statement made in various books on x-rays.[2]

Several investigators[3] have measured the x-ray absorption by chemical compounds and, assuming the above law, have computed the absorption coefficients of the elements present in the compounds. A critical comparison of the results obtained by these experimenters, as pointed out by Taylor[3], indicates that the absorption coefficient for an element may depend upon

[1] Benoist, Journal de physique; **10,** 658, (1901).

[2] W. H. and W. L. Bragg, X-rays and Crystal Structure, 4th ed., p. 41. de Broglie, Les Rayons X, 1922 ed., p. 48. Kaye; X-rays, 4th ed., p. 125. Ledoux, Lebard et Danvillier, La Physique des Rayons X, p. 135.

[3] Auren, Phil. Mag. **33,** 471 (1917); Phil. Mag. **37,** 135, (1919); Phil. Mag. **41,** 733, (1921); Taylor, Phys. Rev. **20,** 709, (1922).

its state of chemical combination with other elements. Further, Bergengren,[4] Lindh,[5] and other investigators[6] recently have shown that for the light elements the wave-length of the absorption limits and of certain emission lines does depend upon the valence of the element. Absorption coefficients for any wave-length must certainly be closely related to emission spectra and absorption limits. Accordingly this investigation was undertaken to study the effect of valence or chemical combination on x-ray absorption.

The absorption by two solutions placed in an x-ray beam was measured. They were then allowed to react chemically and the change in absorption after reaction was measured. Corrections were, of course, made for changes in density. An effect due to chemical combination has been found and measured but no quantitative claim is made for the present results. Further experiments should be performed to determine the value of the effect for different wave-lengths.

Experimental Procedure

For measuring the relative absorption before and after chemical reaction a differential null method[7] was employed. By means of two slit systems

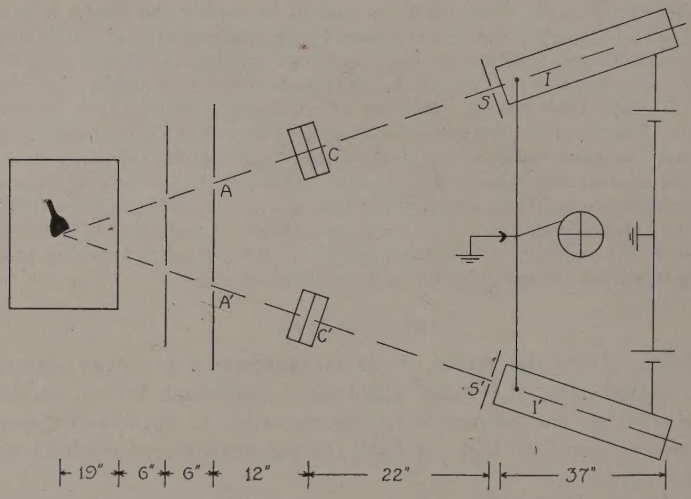

Fig. 1. Diagram of apparatus.

two x-ray beams A and A' from a molybdenum target of a water-cooled Coolidge tube were made to enter two ionization chambers I and I' respectively. These beams if unabsorbed would pass directly through the

[4] Bergengren, C. R. **171,** 624 (1920).

[5] Lindh, C. R.; **172,** 1175 (1921); Fysisk, Tidskr.; **20,** 132 (1922); C. R.; **175,** 25 (1922); Arkiv. f. Matem. Astr. o. Fys.; **18,** 12 (1924).

[6] Tandberg, Arkiv. f. Matem., Astr. o. Fys. **18,** 1 (1924). Chamberlain, Phys. Rev.; **25,** 525 (1925).

[7] Becker, Phys. Rev. **20,** 134 (1922). Read, Phys. Rev. **27,** 373 (1926).

chambers without hitting their walls or the central rods. The projected area of the beam on the back end of ionization chamber I' was approximately 1.5 sq. in. (10 cm^2) at a distance of approximately 9 feet (2.75 m.) from the target. Methyl bromide was placed in the chambers to increase the absorption of the x-rays. The chambers were connected together by rubber tubing so the pressures would equalize. The outside of one chamber was charged positive and the other equally negative. In front of chamber I' was a fixed slit S' 1 in. (2.54 cm) square and in front of chamber I an adjustable slit S easily adjustable to one forty thousandth of an inch. The insulated central rods in the ionization chambers were connected together and to a Compton electrometer. A balance was readily obtained when the electrometer showed no rate of drift. The apparatus was very sensitive and a change in balance of one part in ten thousand, measured in terms of the adjustable slit, could readily be detected.

Equal volumes of the solutions before reaction were placed in a cell C' having two equal compartments separated by either a removable or a fixed partition. In the case of the removable partition the solutions were allowed to react chemically by removing the partition and replacing it after the reaction was completed. In the case of the fixed partition the solutions were poured together into a beaker and after complete reaction the mixture was replaced in the cell. This cell C' was placed in the path of beam A'. Another cell C containing similar solutions was placed in the path of beam A to reduce to a minimum the relative changes in intensity of the two beams due to slight unavoidable fluctuations in the operation of the x-ray tube.

The exact procedure in getting the measurements was as follows. The empty cell C' was placed in beam A'. Then the cell C' plus solutions was placed in beam A'. Next the similar cell C and solutions were placed in beam A. Finally the solutions in beam A' were allowed to react. For each case the slit opening S_0, S, S_1 and S_2 necessary for a balance was obtained.

The cells employed were made from bakelite. Each compartment was 3/8 in. (1 cm) wide. The sides and partition were of bakelite 1/16 in. (1.6 mm) thick. Other cells were used which had the sides and partition of aluminum 0.020 in. (0.5 mm) thick covered with bakelite lacquer, and of hard rubber 1/16 in. thick. Measurements with any cell gave the same results.

The change in balance caused by the reaction may be due to either a change in the absorption coefficient of the solutions or to a change in density or both. Therefore it was necessary that the densities of the solutions before and after reaction be known accurately. For this purpose a Westphal balance was used.

The positions of the solutions relative to the direction of the beam were interchanged to be sure that the effect was not due to scattering caused by the different positions of the elements before and after reaction. This would also eliminate any error due to the compartments not being equal.

A source of alternating current for operating the x-ray tube was obtained by running a rotary converter from a Terrill regulated D. C. generator. Four 100 ampere-hour 6 volt storage batteries were soldered together giving a 12 volt source for the filament. Sufficient time was always allowed for the batteries to approach a constant discharge rate, after which the tube electron current decreased very steadily and at a very slow rate. In all cases the voltage across the tube was 30 K.V. peak.

Measurements were taken using the unfiltered direct beam from the tube. Later an approximately monochromatic beam was obtained by filtering the direct beam through zirconium filters.

All records and computations were made in terms of the adjustable slit width and the density of the solutions before and after reaction.

Formulas

It can readily be shown that for a simple homogeneous mechanical mixture of several elements which are absorbing monochromatic x-rays.

$$\mu=\frac{\mu_a\rho_a+\mu_b\rho_b+\mu_c\rho_c+\cdots}{\rho_a+\rho_b+\cdots+\rho_m+\rho_n+\cdots} \tag{1}$$

where μ is the mass absorption coefficient of the mixture, μ_a, μ_b, etc., are the mass absorption coefficients and ρ_a, ρ_b, etc., are the partial densities in gm per cc for each element present in the mixture. The density of the mixture is equal to the sum of the partial densities. Also it can be shown that for solutions not too concentrated the energy absorbed by a given thickness of the solution is directly proportional to the density.

In the present experiment the rate at which energy I enters the chambers is directly proportional to the slit opening S. (over at least a small range of openings.) i.e.

$$I=KS \tag{2}$$

When no substances are in beam A, if S_0 is the slit opening necessary to effect a balance with the box only in beam A', and S the slit opening with the box plus solutions in the same beam then

$$S=S_0e^{-[\mu_1\rho_1x_1+\mu_2\rho_2x_2]} \tag{3}$$

where μ_1 and μ_2 are the mass absorption coefficients given by Eq. (1), ρ_1 and ρ_2 the density, x_1 and x_2 the thickness of solutions (1) and (2) respectively.

Assuming (1) that the solutions are at the same level in each compartment and (2) that there is no change in either the density or the absorption coefficient it can readily be shown that the transmission after reaction will be the same as before and

$$S=S_0e^{-\mu\rho' x} \tag{4}$$

where μ is given by Eq. (1), $\rho'=(\rho_1+\rho_2)/2$, and $x=x_1+x_2$.

In general a change in density due to the reaction will occur and also there may be a change in μ. This will necessarily cause a change in the

transmission and from Eq. (4) a relation between the change in transmission as measured by the change in slit opening, the change in μ, and the change in density can readily be obtained by differentiating and dividing, remembering that x and S_0 are constant.

$$\frac{dS}{S \cdot 2.303 \log_{10} S/S_0} = \frac{d\mu}{\mu} + \frac{d\rho}{\rho'} \tag{5}$$

dS is the change in slit opening necessary to regain a balance after reaction. $d\rho$ is equal to the difference between the measured density ρ after reaction and ρ'.

The only effect of a change in temperature due to the reaction will be to produce a change in density for Read[8] has shown that the effect of temperature on the absorption coefficient is less than one percent for changes in temperature of 500°C.

The following will show that when a heterogeneous x-ray beam of definite intensity passes through several different materials the amount of energy absorbed is independent of the order in which the materials are placed and if they are mixed it is independent of the order in which the molecules are arranged. The amount of energy absorbed will, however, depend upon the ratio of the intensities of the various wave-lengths present in the beam.

Consider an x-ray beam, composed of two wave-lengths λ_1 and λ_2 of energy $I_{0\lambda_1}$ and $I_{0\lambda_2}$ respectively, which passes through two substances A and B. Let a_1 and a_2, b_1 and b_2 be the absorption constants for substances A and B corresponding to wave-lengths λ_1 and λ_2 respectively. Let I_1 and I_2 be the energy corresponding to wave-lengths λ_1 and λ_2 which gets through the substances. Then

$$I_1 = I_{0\lambda_1}(1-a_1)(1-b_1) \tag{6}$$

$$I_2 = I_{0\lambda_2}(1-a_2)(1-b_2) \tag{7}$$

and the energy of the emerging beam is given by

$$I_1 + I_2 = I_{0\lambda_1}(1-a_1)(1-b_1) + I_{0\lambda_2}(1-a_2)(1-b_2) \tag{8}$$

Equations (6) and (7) are independent of the order in which the beam encounters the molecules of the substances and therefore the energy transmitted which is given by Eq. (8) must be independent of the order in which the beam encounters the molecules of the substances.

The energy absorbed by the substances is given by

$$\begin{aligned}(I_{0\lambda_1} + I_{0\lambda_2}) - (I_1 + I_2) &= (I_{0\lambda_1} + I_{0\lambda_2}) - [I_{0\lambda_1}(1-a_1)(1-b_1) + I_{0\lambda_2}(1-a_2)(1-b_2)] \\ &= I_{0\lambda_1}(a_1 + b_1 - a_1 b_1) + I_{0\lambda_2}(a_2 + b_2 - a_2 b_2)\end{aligned} \tag{9}$$

The average absorption constant for the substances is given by

$$\overline{X} = \frac{(I_{0\lambda_1} + I_{0\lambda_2}) - (I_1 + I_2)}{I_{0\lambda_1} + I_{0\lambda_2}} \tag{10}$$

[8] Read, Phys. Rev. **27**, 373, 1926.

Therefore

$$\overline{X}=\frac{I_{0\lambda_1}(a_1+b_1-a_1b_1)+I_{0\lambda_2}(a_2+b_2-a_2b_2)}{I_{0\lambda_1}+I_{0\lambda_2}} \tag{11}$$

Equation (11) shows that the average absorption constant $\overline{X}$ depends on the ratio of the energy in each wave-length to the total energy in the beam and is only constant provided these ratios are constant. This argument may be extended to include any number of wave-lengths and any number of substances.

Therefore the absorption of heterogeneous x-rays by materials depends upon the energy in the various wave-lengths to the total energy in the beam, and therefore will depend upon the x-ray tube, the voltage applied to the tube, and upon the manner in which the x-rays are filtered.

For a constant ratio between the energy in the various wave-lengths of the x-ray beam the change in the mass absorption coefficient of the solutions due to the chemical reaction can be computed from Eq. (5).

Solutions Studied and Experimental Results

The following reactions were studied using dilute solutions,

$$[KI+I_2]+(2Na_2S_2O_3)\rightarrow KI+2NaI+Na_2S_4O_6. \tag{A}$$

12.7 grams of iodine were dissolved in 1000 cc of a solution of potassium iodide which contained 25 grams of Kl per liter. The solution of sodium thiosulphate contained 25 grams $Na_2S_2O_3\cdot 5H_2O$ per liter. Equal volumes reacted.

$$[K_2Cr_2O_7+6KI]+(6KI+14HCl)\rightarrow 8KCl+2CrCl_3+3I_2+6KI+7H_2O. \tag{B}$$

The solution of potassium dichromate contained 5 grams $K_2Cr_2O_7$ per liter. The solution of potassium iodide contained approximately 40 grams KI per liter and the solution of HCl contained 10 grams HCl per liter. The reaction was the equivalent of equal volumes of these solutions reacting.

$$[NaOH]+(HCl)\rightarrow NaCl+H_2O. \tag{C}$$

The solution of sodium hydroxide contained 28 gms NaOH per liter. The solution of HCl contained 26 gms HCl per liter. Equal volumes reacted.

$$[KOH]+(HCl)\rightarrow KCl+H_2O \tag{D}$$

The solution of potassium hydroxide contained 28 grams KOH per liter and the solution of HCl contained 18 grams HCl per liter. Equal volumes reacted.

$$[I_2 \text{ in } 70\% \text{ alcohol}]+(2Na_2S_2O_3)\rightarrow 2NaI+Na_2S_4O_6. \tag{E}$$

12.7 grams of iodine was dissolved in 70% solution of alcohol making a liter of solution. The solution of sodium thiosulphate contained 25 grams of $Na_2S_2O_3\cdot 5H_2O$ per liter. Equal volumes were used.

In each case the substances in square brackets were initially in one compartment of the cell and the substances in round brackets in the other compartment.

Sample of Calculations

The following is a complete sample set of data and computations on Reaction A.

Voltage across tube: 30 kv peak.
X-ray tube electron current: 10.4 milliamperes.
Sensitivity of electrometer: 2000 mm per volt.
Volume of each solution used: 160 cc.

S_0:	1.2494″	1.2495″	1.2500″	Average	1.2496
S:	0.1720	0.1717	0.1717		0.1718
S_1:	0.9881	0.9883	0.9885	0.9882	0.9883
S_2:	0.9950	0.9953	0.9953	0.9954	0.9952

S_1 is the slit opening with similar solutions in both beam A and B before reaction and S_2 is the slit opening after the solutions in beam A have reacted.

Density of $[I_2+KI]=\rho_1=1.0266$ gm per cc.
Density of $(Na_2S_2O_3)=\rho_2=1.0124$ gm per cc.
Density of solution after reaction $=\rho=1.0182$ gm per cc.

$$\rho'=(\rho_1+\rho_2)/2=1.0195 \text{ gm per cc.}$$
$$d\rho=\rho'-\rho=-0.0013 \text{ gm per cc.}$$
$$dS=S_1-S_2=-0.0069''.$$
$$\frac{dS}{2.303\, S_1 \log_{10}(S/S_0)}=\frac{d\mu}{\mu}+\frac{d\rho}{\rho'}$$
$$d\mu/\mu=-0.0022.$$
$$\text{Change in } \mu=-0.22\%.$$

Table I

Values of the change in absorption coefficient resulting from chemical reaction. The last line in the table gives the average percent change in μ for each type of reaction studied. In case 1 the x-ray beam passed through the substance in square brackets first, and in case 2 it passed through the substances in round brackets first.

Reaction A Unfiltered beams (percent)		Reaction A Zirconium filtered beams (percent)		Reaction B Unfiltered beams (percent)		Reaction C Unfiltered beams (percent)		Reaction D Unfiltered beams (percent)		Reaction D Zirconium filtered beams (percent)		Reaction E Unfiltered beams (percent)	
1	2	1	2	1	2	1	2	1	2	1	2	1	2
−.36	−.17	−.22	−.33	+.27	+.15	+ 21	−.13	−.06	+ 19	−.02	+.09	−.40	−.23
−.29	−.23	−.18	−.19	.45	20	.18	−.00	−.05	.00	+.09	.09	− 35	−.31
−.30	−.42	−.64	−.41	.31	.32	.18	−.09	−.16	.04	−.18	.20	−.36	−.23
−.35	−.22	−.33	−.18	.21	.21	.14	−.05	−.09	.05	−.06	.13	−.31	−.23
−.22	−.31	−.59	−.27	.20	.22	.12	−.18	−.13	.07	+.05	−.06	− 36	−.29
−.21	−.40	−.25	−.23	.18	.21	.11	−.20	−.17	.01	−.10	+.15	−.28	−.34
−.10	−.15	−.44	−.24	.48	.35	.12	−.12					−.24	−.38
−.27	−.21	−.43	−.76	.33	.31							−.35	−.54
−.08	−.20		−.35	.32	.31							−.53	−.54
−.23	−.16			.22	.25							−.54	−.50
	−.14			.21	.25								
				.12	23								
				.12	.16								
				.17	.17								
−.24	−.24	−.33	−.38	+.26	+.24	+.15	−.11	−.11	+.06	− 04	+.10	−.37	−.34
±.03	±.03	±.04	±.04	±.03	±.02	±.02	±.02	±.02	±.02	±.03	±.03	±.02	±.03
−(.24 ± .03)		−(.36 ± .04)		+(.25 ± .03)		+(.02 ± .02)		−(.03 ± .02)		+(.03 ± .03)		−(.36 ± .03)	

In reaction (A) and (E) the iodine changes its valence from 0 to -1 and the valence of the sulphur increases positively. In reaction (B) the iodine changes its valence from -1 to 0 and chromium from 6 to 3. In reaction (A) the amount of iodine per sq. cm in the beam before and after reaction was .032 gms of which .013 gms changed its valence. In reaction (B) the amount of iodine per sq. cm in the beam before and after reaction was .031 gms of which .013 gms changed its valence. In reaction (E) the amount of iodine per sq. cm in the beam before and after reaction was .013 gms and all of it changed its valence.

In reactions (C) and (D) the valence of all elements in the beam is the same after reaction as before. For these determinations a cell with a removable partition was used and the compartments were not exactly equal. Equal volumes were used and the solutions were not at the same level which explains why the effect is positive for one case and negative for the other. The average of the results being practically zero (at least within experimental error) indicates that probably the effect due to the reaction is approximately zero.

The results in general indicate that the mass absorption coefficient for an element depends upon its valence and is therefore different for different states of chemical combination. Computations from known absorption coefficients show that the absorption by the iodine in the beam was several times (approximately 15 times) that due to either the sulphur or the chromium, which indicates that probably the measured effect is practically all due to the iodine. This is also indicated by the results for reaction (E) where all the iodine changed its valence.

The larger effect from reaction (A) when using the filtered beam may indicate that the effect is different for different wave-lengths of x-rays, or it may be caused by the change in the ratio of the intensities of the various wave-lengths present in the beam as indicated by Eq. (11). The filtered x-rays when using a zirconium filter are at best only approximately monochromatic.

Theoretical Explanation of Results and a Comparison with the Results of Experiments Indicating a Dependence of the Wave-Length of Absorption Limits and Emission Spectra Upon Valence.

Experimental results[9] show that on the short wave-length side of the K absorption limit the atomic absorption coefficient can be represented by the following approximate formula

$$T_a = CN^4\lambda^3 . \qquad (1)$$

where T_a is the atomic absorption coefficient; C is a constant; N is the atomic number; and λ is the wave length of the x-rays. On the long wave-length side of the limit the formula has practically the same form excepting the exponents may be slightly different, and C is different.

[9] Richtmyer, Phys. Rev. **17**, 264 (1921); Richtmyer & Warburton, Phys. Rev. **21**, 721 (1923).

For the K absorption limit, Moseley's law may be written in the form

$$\lambda_K = K_1/(N-b)^2 \qquad (2)$$

where λ_k is the wave length of the absorption limit, K_1 is a constant, N is the atomic number, and b is the screening constant.

If Eq. (2) be combined with Eq. (1) there results[10]

$$T_a' = C'N^4/(N-b)^6 \qquad (L)$$

where T_a' is the atomic absorption coefficient just at the short wave-length side of the absorption limit.

Differentiating Eq. (3) with respect to T_a' and b there results

$$dT_a'/T_a' = 6db/(N-b) \qquad (4)$$

which at once indicates that if the screening constant increases the value of T_a' increases, and vice versa.

The results of several experimenters[4,5,6] show that in general the absorption limit comes at a shorter wave length when the element is in the combined state than when it is in the free state, also that the wave length is different when the element is combined under different valences. Usually the higher the valence the shorter the wave length. On the basis of Moseley's law, equation (2), this must mean that the value of the screening constant, when the element is in the combined state, is less than when the element is in the free state since the atomic number of the element is certainly the same whether the element is free or combined.

Experimental results[11] also show that the wave length of the emission lines depends upon the valence of the element. The wave length is longest when the element is in the free state and appears to decrease as the valence increases in the combined state. This again, on the basis of Moseley's law, must mean that the screening constant when the element is in the free state is greater than when it is in the combined state.

By comparing these results with equation (4), it becomes apparent that at the absorption limit the absorption coefficient for an element when in the combined state must be less than when it is in the free state. It seems reasonable to think that the same may be true at any wave length which would explain qualitatively at least, the present results and show that they are in accord with the experiments[4,5,6,11] mentioned above.

Criticism of Experiment and Result

For the work described the balance method is good. However the intensities of the two beams were not exactly the same and changes would necessarily cause errors in the observations. These changes were reduced to a minimum by having similar solutions in each beam. The accuracy of taking slit readings was about 2×10^{-4} in. and of taking density measurements about 2×10^{-4} gm per cc.

[10] Richtmyer, Phys. Rev. **27**, 1 (1926).

[11] Ray, Phil. Mag. **49**, 168 (1925); **50**, 505, (1925).

An obvious suggestion might be that the effect was due to a difference in the scattering before and after reaction, but since the measured effect was the same no matter which solution the beam passed through first it seems very probable that it was not due to a difference in scattering. It is very difficult to say whether the effect was caused by the short or long wave lengths present in the beam.

Conclusions

The results appear to indicate that the x-ray absorption by an element depends upon its valence and therefore upon its state of chemical combination. In the case of Iodine they seem to indicate that its absorption may be greater in the free state than in the combined state.

It gives me great pleasure to thank Professor F. K. Richtmyer for his many valuable suggestions and his keen interest during the progress of this experiment. He suggested the study.

Rockefeller Hall,
Cornell University.
June, 1926.*

* Received February 23, 1927—Editor.